

# Fluid-bicontinuous emulsions stabilized by colloidal particles

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## Abstract

Using controlled spinodal decomposition, we have created a fluid-bicontinuous structure stabilized by colloidal particles. We present confocal microscopy studies of these structures and their variation with kinetic pathway. Our studies reveal a rigid multilayer of colloidal particles jammed at the interface which prevents the liquids demixing for many hours. The arrangement of two-fluid domains, interpenetrating on the meso-scale, could be useful as a microreaction medium.

Emulsions are metastable soft materials of great industrial importance. The liquid-liquid interface is conventionally stabilized by amphiphilic surfactant molecules; the behavior of the resulting systems is well understood [1]. A less common variant, with the surfactants replaced by colloidal particles or nanoparticles [2, 3, 4], was discovered over a century ago [5]. The colloids are much more strongly pinned to the interface than are the surfactant molecules. Recent research has begun to focus on the fundamental

understanding of colloid stabilized emulsions, which show strongly history-dependent properties [3, 6, 7]. This exemplifies a growing interest in the behavior of materials that are irreversibly arrested far from equilibrium [8] (glasses, gels, etc.).

The trapping of solid particles at a liquid-liquid interface is governed primarily by the wetting angle  $\theta_w$  of the liquid-liquid-solid contact line [3]. This in turn depends on the surface chemistry (wettability) of the colloid, and on the distance from the critical point for liquid-liquid demixing [9, 10], at which the liquid-liquid interfacial tension  $\gamma$  vanishes. Maximal stabilization occurs close to the neutral wetting condition ( $\theta_w = 90^\circ$ ); a colloid of radius, say,  $r = 0.25 \mu\text{m}$  then reduces the interfacial energy by [3]  $\Delta G_{int} = \pi r^2 \gamma (1 \pm \cos(\theta_w)) \sim 10^4 k_B T$  (for a typical  $\gamma \sim 1 \text{ mN m}^{-1}$ ) so that adsorption to the interface cannot be reversed by Brownian motion [3]. If such colloids are vigorously mixed in a pair of immiscible liquids, stable emulsion droplets will form; the wetting angle and the relative phase volumes determine which liquid becomes the dispersed phase [11]. As well as emulsification by conventional mixing [12, 2, 3, 4], dialysis [13] and microfluidic emulsification [14] also lead to droplets.

In a recent study [7] we discovered a quite different route to particle-stabilized droplet emulsions based on binary-fluid phase separation. Silica particles were initially dispersed in the single-fluid phase of alcohol-oil mixtures [15]. Following a shallow quench, the liquids separate via nucleation (Fig. 1). The nuclei coarsen until they are covered with a densely packed layer of particles. Figs. 2a & b show the resulting droplets of hexane stabilized by a multilayer coating of colloids. The colloid-laden interfaces are rigid, with relatively high elastic moduli; these structures are stable for at least a day. Under certain conditions, droplets are aspherical with frozen shapes [7] (Fig. 2c & d). This is the result of coalescence between incompletely coated droplets. Some multiple emulsion (droplet within droplet) formation is also evident.

In this letter we report the use of this experimental approach to create a quite different class of structures. Specifically, we show that by performing a deep quench at phase volumes close to 50:50 in colloid-doped binary-fluid systems with a near-symmetric phase diagram (Fig. 1), bicontinuous structures form, and are stable. In these bicontinuous emulsions, as with the droplet emulsions formed by shallow quenches [7], the liquid-liquid interface is coated by an immobile layer of colloidal particles. With our protocols, this layer is several particles thick; similar layers are seen in silica colloid-stabilized droplet emulsions [16]. Though not yet conclusive (due primarily to the thin-slab geometry of our samples) our

quenches promise the creation of a fully three-dimensional, bulk solid material simultaneously permeable to two immiscible solvents, with potential uses as a continuous-flow microreaction medium [17, 18].

Our experimental results confirm in broad outline, though not in every detail, a theoretical scenario for the formation of such materials presented by Stratford *et al.* [18], who dubbed them ‘Bijels’ (bicontinuous interfacially jammed emulsion gels). These authors report computer simulations that run for about 300 ns, showing sequestration of a monolayer of neutrally wetting nano-colloids, and drastic curtailment of binary-fluid demixing, on that time scale. Extrapolating boldly by some nine decades in time, it was suggested in [18] that Bijels should remain arrested, as metastable, three-dimensional bulk solids, on macroscopic timescales.

The structures we have created strongly contrast with bicontinuous microemulsions [19], which are analogs in which the particle layer is replaced by soluble surfactants. The bicontinuous surfactant layers continuously break and reform; microemulsions are hence equilibrium structures and stable only under a limited range of thermodynamic parameters. Our bicontinuous structures, stabilized by interfacially jammed colloids, appear to be robust metastable states due presumably to the large energy barrier holding the colloids in place.

The binary liquids used here are methanol-hexane (with upper critical solution temperature – UCST 33.2° C for 27.5:72.5 alcohol:oil by volume) and ethanol-dodecane (with UCST 12.5° C for 36.1:63.9 alcohol:oil). The phase diagrams resemble Fig. 1. For all the experiments described in this letter a volume fraction half-way between critical and 50:50 was chosen (that is 39:61 methanol:hexane and 43:57 ethanol:dodecane). This is a compromise between equal volumes and the critical composition, and, was chosen to favor the formation of stable bicontinuous structures. The silica colloids ( $r = 0.220 \pm 0.007 \mu\text{m}$ ) were synthesized using the Stöber procedure [20]. A single batch of colloids was used for all of the results presented here. The surface chemistry was modified using the recipe described in ref. [21]. For methanol-hexane,  $10^{-2}$  M of the silanizing agent (dichlorodimethylsilane - DCDMS) gave close to neutral wetting (as estimated from the behaviour of macroscopic emulsion droplets). For ethanol-dodecane,  $10^{-1}$  M of DCDMS was used.

Prior to quenching, the liquids were combined in an incubator (at 45° C for methanol-hexane and 28° C for ethanol-dodecane). The colloids (2% by volume) were dispersed using an ultrasound processor (Sonics & Materials) operating at 20 kHz for 2 minutes at 2–3 W power. The sample cells,  $0.2 \times 4.0 \times 50.0 \text{ mm}^3$

(VidroCom), were filled using capillary action. The filled cells were then quenched into the demixed regime in various different ways. The end-point temperature of the quench was chosen to avoid freezing of either of the liquids.

In Fig. 3 we present confocal microscopy images (rendered using the ImageJ software package [22]) of bicontinuous structures created by deep quenching of a methanol/hexane mixture doped with colloidal silica particles with near-neutral wetting. The sample shown in Fig. 3(a) was obtained by first dipping it in liquid nitrogen for 5 seconds and then cooling it in a CO<sub>2</sub> bath (-78° C) for 5 minutes. The sample shown in Fig. 3(b) was obtained by cooling it in liquid nitrogen for 30 seconds before submerging it in the CO<sub>2</sub> bath. The small differences in fabrication procedure appears to be reflected in a smoother arrangement of colloids on the interface. The images (Fig. 3) are for a thin slab of material (thickness 200  $\mu\text{m}$ ) and show a particle-coated interface between the two fluid domains. This interface appears rough and lumpy, with the coating of particles about six colloids thick over much of its area (thicker in the lumpiest regions). The structure is bicontinuous: there are connecting pathways of both fluids across both long and short dimensions of the cell. This requires the presence of free-standing fluid necks within the slab, and at least two of these are visible in Fig. 3(a). These necks show clear departures from the condition of constant mean curvature required for static mechanical equilibrium of a fluid-fluid interface (Fig. 3(b)).

Such variations in mean curvature are sustainable only by a rigidly frozen interface, or a fluid film with near-zero interfacial tension (dominated by curvature elasticity). In the latter case, the surface irregularities visible in Fig. 3 would fluctuate in time; this is not seen. We infer that the colloidal layer is rigid on the timescale of hours over which these observations were made. Were the interface to be fluid with finite tension, structures like the neck in Fig. 3(b) would rapidly pinch off via the Rayleigh-Plateau instability [18].

Although our bicontinuous structures remain stable for more than a day, in some cases a slow evolution of the local structure is observable on this time scale. This could be due to residual ‘aging’, as the structure lowers its energy locally by slight rearrangement [18]. Alternatively, it could mean that the colloidal layer is not fully solid, but instead a viscoelastic fluid film. This would allow coarsening of the structure to slowly proceed indefinitely, in contrast to the arguments of Stratford *et al.* [18], who suggested that the interfacial stresses should cause a colloidal monolayer to undergo a glass transition into an amorphous

solid. The amorphous interfacial films we observe are thicker than a monolayer, distributing these stresses over additional particles and possibly reducing the propensity to jam the layer fully.

Our work shows that, at least for the materials and sample geometries studied here, a bicontinuous interfacial structure indeed forms, and remains arrested for periods of hours or days. As detailed above, we have found stable bicontinuous structures in two distinct pairs of binary liquids, requiring different surface treatment of the colloids and different quenching schedules. Our results can be combined with those of our previous study of shallow quenches [7] (Fig. 2a & b) to illuminate the role of the kinetic pathway in structure formation. In droplet emulsions, coalescence usually proceeds at a diameter-dependent rate until kinetic arrest occurs on complete surface coverage [23]. In our bicontinuous quenches we cannot resolve the coarsening dynamics, but the final length scale of the arrested state should be dictated by the colloid volume fraction  $\phi_v$  and the thickness of the stabilizing layer. For a layer  $n$  colloids thick, the typical distance between interfaces [18] is  $\xi \sim nr/\phi_v$ . This scaling, which should apply also in the slab geometry, is broadly confirmed by varying  $\phi_v$  (Fig. 4). (Droplet emulsions permit a broader size distribution which can also depend on interfacial curvature; no simple scaling is expected in that case.) The sample shown in Fig. 4(a) was quenched by submerging it in liquid nitrogen for 30 seconds and then in an ice bath for 6 minutes. The deep quenches we employ here seem to be essential in promoting fluid bicontinuity [24], which is not seen in emulsification by mixing [3] even very close to  $\theta_w = 90^\circ$ . Although shallow or slow quenches favor conventional droplet emulsions, warming such an emulsion back toward the miscible region of the binary fluid phase diagram (Fig. 1) results in an enhanced tendency for droplets to coalesce. Other studies [7] show that the colloid-stabilized droplets can remain intact well above the phase boundary. Such warming, followed by a second quench, induces the formation of fused droplets (Fig. 2c & d). The cusps formed at the junction between these droplets appear stable for long periods of time, again signifying solidification of the colloid film. Controlled coalescence of such droplets may offer an alternative route to the creation of bicontinuous structures.

Our fluid-bicontinuous structures exemplify a more general phenomenon. Formation of many composite soft materials [25, 26, 27, 28, 29, 30, 31] involve the co-evolution of a host system that undergoes a phase transition (e.g., liquid crystals [25, 26], binary fluids [27, 28], polymer blends [29, 30, 31]) with a dispersed constituent that alters or arrests that process (e.g., colloids [26, 30, 31, 28], polymers [25, 27], block copolymers [29]). On cooling, the host fluid begins to demix or form an ordered phase. The dispersed

component then segregates either within a preferred phase or at the interface. This segregation requires partial phase ordering of the host, but then prevents this from going to completion. In our case, the true equilibrium state comprises full macroscopic phase separation (even with the particles present [18]); but this state cannot be reached due to quasi-irreversible trapping of colloids at the liquid-liquid interface. This pathway has similarities to hardening of metals by impurities trapped at domain boundaries. It also resembles the formation of colloid-nematic gels (although these are not bicontinuous) [26], and might result in equally surprising bulk rheological properties [17].

Beyond possible applications as microreaction media or rheologically active materials [17], there are fundamental reasons to further explore the properties of our fluid-bicontinuous emulsions. First, changes to the phase transition kinetics due to the colloidal particles may arise: nonuniversal behaviour was found for phase-separating polymer blends with surfactant [29]. Second, the colloidal films themselves represent interesting low-dimensional systems [32, 33] whose glass-transition physics is coupled to a non-Euclidian curved space. Finally, alternative routes to the formation of arrested structures might involve pressure quenches, controlled coalescence, or highly energetic mixing. These could enlarge the range of length scales and of fluid pairs for which bicontinuity is possible.

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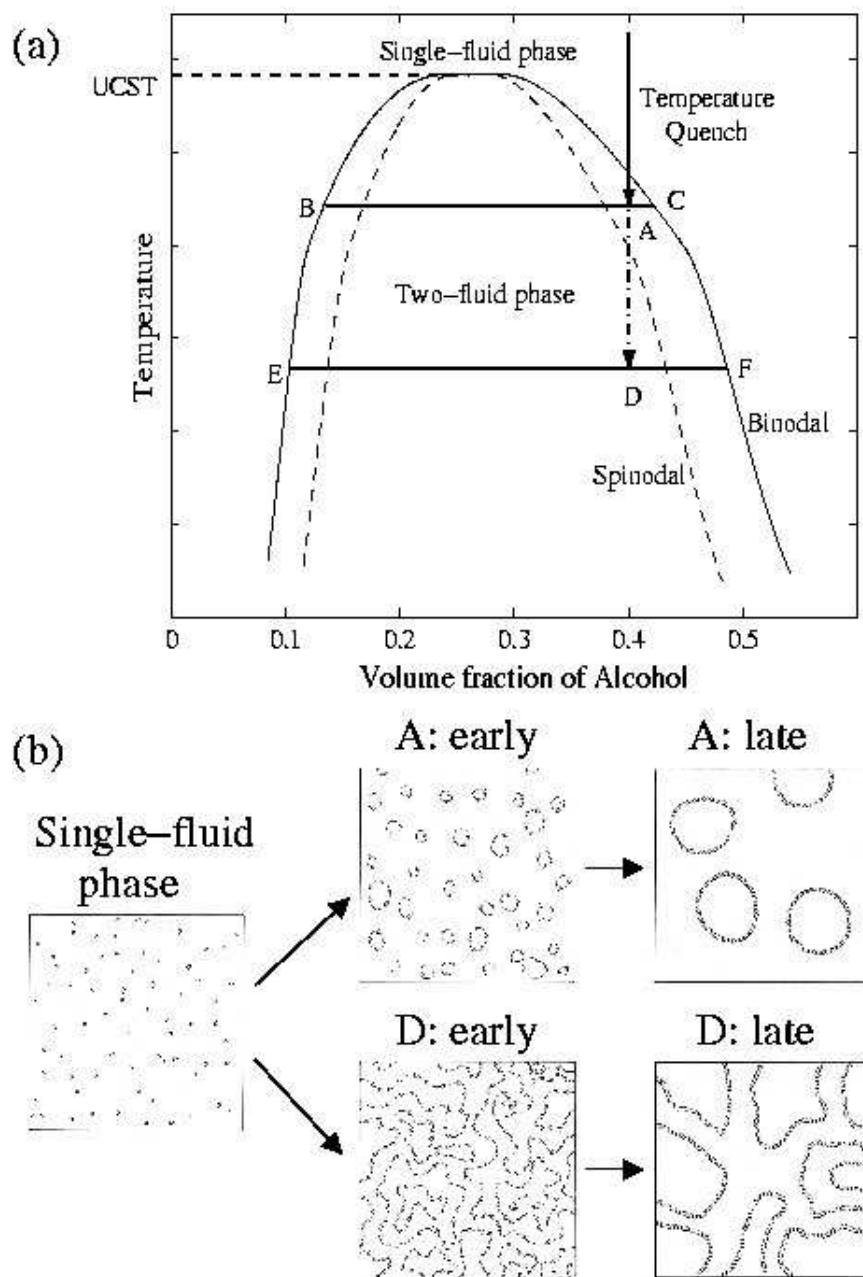


Figure 1: (a) Generic alcohol-oil phase diagram showing binodal (solid line) and spinodal (dashed line). The liquids are miscible above the upper critical solution temperature (UCST). A shallow quench is pathway A (top (b)): liquids separate via nucleation and a colloid-stabilized droplet emulsion forms. The separated liquids have compositions B and C. A deep quench is pathway D (bottom (b)): liquids separate via spinodal decomposition leading to a fluid-bicontinuous gel. The separated liquids have compositions E and F.

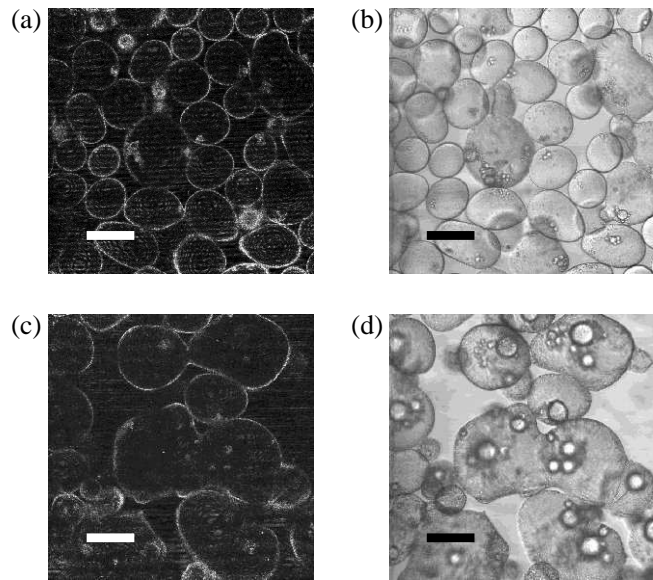


Figure 2: (a) Confocal and (b) bright-field microscopy images of a hexane-in-methanol emulsion stabilized by silica colloids [15]. Fabrication corresponds to pathway A in Fig. 1. Confocal images show the interface while bright-field images show the contents of the droplets. (c) Confocal and (d) bright-field microscopy images of the same emulsion after it has been reheated then quenched to 0° C. These images were all captured at room temperature and the scale bars are 100  $\mu\text{m}$ .

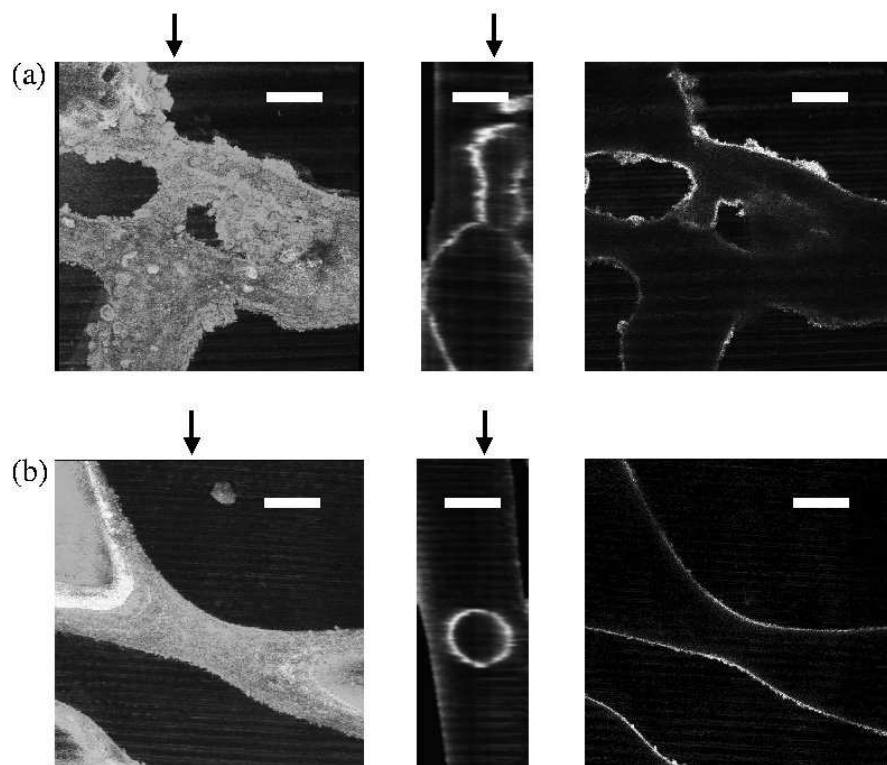


Figure 3: Left: Rendered confocal images of 3D structures viewed from above; center: vertical slices corresponding to the position of the arrow on the left; right: horizontal slice through the confocal stack on left (corresponding to the position of the arrow in the center). (a) Arrested bicontinuous structure. (b) An isolated fluid neck, ending at contact lines with the glass plates confining the sample, stabilized by a colloidal multilayer. The creation of these structures corresponds to pathway D in Fig. 1. All the images were recorded at room temperature. Scale bars  $100\ \mu\text{m}$ .

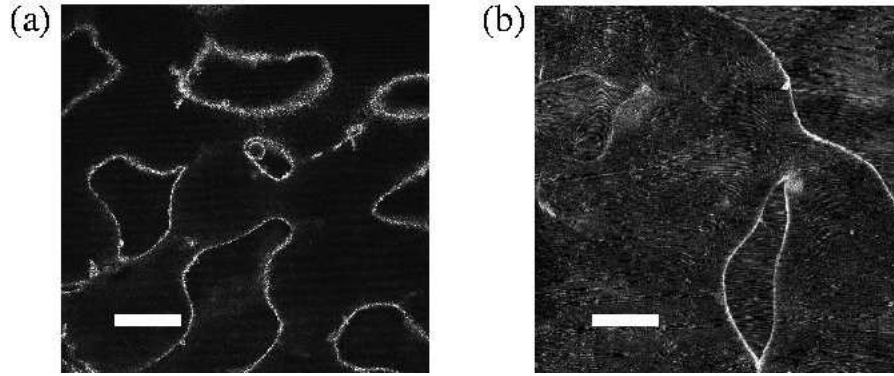


Figure 4: (a) Confocal image recorded at 0° C (using a cold stage, Linkam Scientific Instruments) through an ethanol-dodecane structure stabilized by  $\phi_v = 0.02$  silica colloids (preparation described in the text). The characteristic separation between interfaces is  $\xi \sim 150 \mu\text{m}$ . (b) Confocal image recorded at room temperature of a methanol-hexane structure stabilized by  $\phi_v = 0.01$  silica colloids [15]. The characteristic separation between interfaces is  $\xi \sim 300 \mu\text{m}$ . Scale bars  $100 \mu\text{m}$ .